A CONTRIBUTION TO THE STUDY OF THE RELATION BETWEEN COLOR AND CONSTITUTION IN THE TRIPHENYLMETHANE SERIES.

BY

LUCAS PETROU KYRIAKIDES.

A THESIS SUBMITTED TO THE FACULTY OF THE DEPARTMENT OF LITERATURE, SCIENCE, AND THE ARTS OF THE UNIVERSITY OF MICHIGAN FOR THE DEGREE OF DOCTOR OF SCIENCE.

ANN ARBOR, MICH.

1909.

EASTON, PA.:
ESCHENBACH PRINTING COMPANY.
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The following investigation was carried out in the laboratory of Organic Chemistry of the University of Michigan.

The work was undertaken at the suggestion of Professor M. Gomberg.

I wish to acknowledge my indebtedness to Professor Gomberg for his interest in the work, and his friendly suggestions and criticisms.

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I. INTRODUCTION.

A. W. Hoffman,[1] the discoverer of fuchsine, had assigned to this dye the empirical formula $C_{20}H_{20}N_3Cl$, and to rosaniline $C_{20}H_{21}N_3O$, stating that the first was the hydrochloride, and the second the hydroxide of a tertiary amine, $C_{20}H_{19}N_3$. Caro and Graebe[2] proved that rosolic acid and rosaniline were the derivatives of one and the same hydrocarbon. Further, from some reactions of the acid, they concluded that the latter belonged to the class of the quinones. Their formula, however, failed to explain the function of the groups containing the oxygen atoms. E. and O. Fischer[3] were the first to give a general constitutional formula for the amido and hydroxyl derivatives of triphenylmethane. They showed that para rosaniline—a tertiary alcohol—was unstable in presence of acids, and that in its salts it lost a molecule of water. They explained this fact by the hypothetical amine of the following constitution: $(H_2NC_6H_4)_2 : C\begin{smallmatrix} C_6H_4 \\ | \\ NH \end{smallmatrix}$, where the anhydration took place between one of the amido groups and the carbinol hydroxyl, thus linking the imido group to the central carbon atom. The peroxide quinone formula of Graebe explained in this case the color of the salts.

Later, Nietzki[4] modified the quinone formula as follows: R = = C =, this representing the chromophore group of the triphenylmethane dyes.

The discovery of "Triphenylmethyl" by Gomberg,[5] gave a new impetus to the study of the triphenylmethane derivatives. Its study led to the discovery of the double salts of triphenylchlormethane. Norris and Sanders,[6] Gomberg,[7]

[1] Proc. Roy. Soc., **12,** 2 (1862).
[2] Ann., **179,** 184 (1875).
[3] *Ibid.*, **194,** 242.
[4] Farbstoffe, I Auflage, 88 (1889).
[5] J. Am. Chem. Soc., **22,** 757 (1900).
[6] Am. Chem. J., **25,** 55 (1901).
[7] J. Am. Chem. Soc., **23,** 497 (1901).

and Kehrmann and Wentzel[1] described such double salts, all intensely colored.

Kehrmann assigned to triphenylmethyl chloride in the double salt, the following constitution: $(C_6H_5)_2 : C:$ stating that the color and the salt-like character of the carbinol chloride were due to the above desmotropic modification. He also pointed out, that the basic character of the triphenylmethyl radical was due to the divalent carbon atom of the quinoid nucleus in the para position to the methane carbon atom. Baeyer[2] explained the color of the carbinol halide salts on the assumption that triphenyl methane as such could give colored salts. This property of a substance he termed "Halochromy." The salts he called "carbonium salts" of triphenylmethyl—the central carbon atom being responsible for the basic properties of the hydrocarbon. This view seemed to do away with the necessity of a chromophore group—such as the quinoid.

Gomberg[3] then showed that the carbinol halides dissolved in ionizing solvents—such as sulphur dioxide—with color and conducted electricity. The conclusion drawn was in support of Baeyer's halochromic theory. The color of the solutions was thought to be due to the positive ion. The ester formula seemed now pretty well established.

Baeyer and Villiger[4] having succeeded in isolating a number of phenylimids, analogous to the assumed Homolka base, expressed the conviction that the basic dyes did contain the quinonimid group. However, they held that the constitution of the simple and halogenated triphenylmethane salts, whether colored or not, had to be expressed by the ester formula $R_3C.X$. In a previous article,[5] they had based this conviction on the behavior of tri-para-anisyl-chlormethane, which treated with sulphuric acid, did not liberate

[1] Ber., **34,** 3815 (1901).
[2] *Ibid.*, **35,** 1189 (1902).
[3] *Ibid.*, **35,** 2405 (1902).
[4] *Ibid.*, **36,** 2774; **37,** 597, 2848 (1904).
[5] *Ibid.*, **35,** 1189 (1902).

methyl alcohol, in spite of the fact that the solution was intensely colored. Later, having seen no necessity for such a behavior, Baeyer[1] prepared the tri-*p*-halogenated derivatives of triphenyl carbinol, and changed these into the sulphates. He then premised, that if quinoidation did really take place, the halogen in the quinoid group would behave differently from those in the benzene nuclei. Consequently, silver acetate ought to replace the halogen by the acetic acid radicle. Experiment, however, did not sustain the assumption. The conclusion was that the chromophore group in the colored acid sulphate, $(ClC_6H_4)_3C.O.SO_3H$, was the same as that in triphenyl carbinol itself—the halogen atoms playing the function of auxochrome groups. The above observation led Baeyer to the development of the "Carbonium" theory. He taught that one and the same substance could exist in two states: one, the colorless and non-ionizable; the second, the colored and ionizable. He also stated that this difference lay in the valence. The valence peculiar to the colored salts he called the *Carbonium* valence, and designated it by a zigzag line—$(C_6H_5)_3$ C∼∼Cl. The ordinary valence peculiar to the colorless chloride, he designated by the straight line, $(C_6H_5)_3C$—Cl. Further, to be consistent with this new theory of his, he stated that the color of the imines was due *primarily* to the *double carbonium* linkings between the quinoid nucleus and the methane carbon atom. The constitution of parafuchsine might be that given to it by Rosenstiehl with this peculiar valence $(H_2NC_6H_4)_3C{\sim\sim}Cl$—the strongly positive character of the triamino-triphenylcarbinol radical inducing the change of the ordinary to the carbonium valence.

Gomberg and Cone[2] gave positive experimental proof in regard to the quinoid structure of the simple and halogenated triphenylcarbinol salts. They observed that molecular silver abstracted from the *p*-halogenated halides in benzol solution, not only the labile chlorine, but also from a fraction to a whole atom of the nucleus halogen. Hence, they thought

[1] Ber., **38,** 569 (1905).
[2] *Ibid.*, **39,** 3274 (1906).

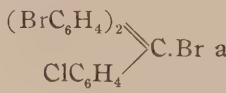
that one of the phenyl groups under the influence of the silver assumed a different function from the rest—this function being probably that of a quinoid group. Furthermore, Gomberg[1] showed that the same halides in benzol solution, treated with silver sulphate, gave intensely colored salts. Excess of silver sulphate was found to abstract, after prolonged shaking of the organic sulphate with the inorganic salt, amounts of the para halogen varying up to one atom. The negative results of Baeyer[2] he explained by the inhibitive effect of sulphuric acid, which the latter had used as a component of his solvent. Again, he subjected the same halogenated derivatives to the action of silver chloride in sulphur dioxide. He observed that in the case of the tri-*p*-brom-derivative, all the three bromine atoms could be replaced one after another by chlorine. Here the quinoidation must have extended to all three nuclei. Gomberg explained this phenomenon by the equilibrium which existed between the two isomers, and the subsequent disturbance of the same by the substitution of chlorine for bromine. In conclusion he added,"The colored chlorides and sulphates are salts which are derived from the *quino-carbonium* base R_2C: ."

Baeyer[3] then came to the defense of his halochromic theory with the following argument: If the double salts did really owe their color to the tautomeric modification of triphenyl methyl, then the ferric chloride double salts of the tri-*p*-chlor, and tri-*p*-brom derivatives ought to have the same quinoid part, $(ClC_6H_4)_2 : C$: + $FeCl_3$ and $(BrC_6H_4)_2 : C$: + $FeCl_3$. Hydrolysis of each, then, ought to liberate the same amount of chlorine or bromine, provided the non-quinoid halogenated phenyl groups did not exert any directive influence. Experiment, however, showed that the bromide of the trichlor compound

[1] Ber., **40,** 1847 (1907).
[2] *Ibid.*, **38,** 569 (1905).
[3] *Ibid.*, **40,** 3083 (1907).

gave only bromine, while the chloride of the tribrom derivative liberated only chlorine. The positive results of Gomberg he explained on the assumption that silver sulphate in presence of an insufficient amount of sulphuric acid broke up the molecule completely.

Baker,[1] "regarded the constitution of the salts of pararosaniline with one equivalent of acid as $(NH_2.C_6H_4)_2C$." This formula, according to him, explained most satisfactorily the general reactions of the compound.

Tschitschibabin[2] obtained the same results as Baeyer, but independently of him. Furthermore, he reasoned that if tautomerization took place in sulphur dioxide, by evaporating off the solvent, in the case of $(BrC_6H_4)_3C.Cl$, he ought to get a mixture of the two isomers:  and $(BrC_6H_4)_3.C.Cl$. Consequently, he warmed the sulphur dioxide solutions of the above chloride for 20–40 hours, but evaporation of the solvent did not show a trace of the first isomer. These results, the author stated, supported the view of Baeyer.

Gomberg,[3] finally, succeeded in proving experimentally that the triphenyl carbinol halides in sulphur dioxide have the quinoid constitution. He dissolved the para-halogenated derivatives in this solvent, and after several days, evaporating off the solvent, he obtained a mixture of the two isomers, which Tschitschibabin had failed to detect.

The present work was undertaken with the object of studying the nature of the double salts of the triphenyl methane halogenated derivatives, their relation to the phenomena of quinoidation, and of determining the effect of oxygen in connection with the same phenomena.

[1] J. Chem. Soc., **91**$_2$, 1490 (1907).
[2] Ber., **40**, 3965 (1907).
[3] *Ibid.*, **42**, 406 (1909).

II. SYNTHESIS OF MATERIALS.

Di-p-brom-p-chlor-triphenylcarbinol.

This substance was synthesized from *p*-chlor-iodo-benzene and *p*-dibrom-benzophenone, by means of Grignard's reaction. *P-chlor*-iodo-benzene was prepared from *p*-chloraniline by means of Sandmeyer's[1] reaction. *P*-chloraniline[2] was prepared from acetanilid by first chlorinating and then saponifying the latter.

For the Grignard reaction 2.4 grams of magnesium were heated with an ethereal solution of 30 grams of *p*-chlor-iodo-benzene, until the metal was completely dissolved. The Grignard reagent was then cooled, and a benzol solution of 29 grams of di-*p*-brom-benzophenone was added. After boiling for a couple of hours, the reaction mixture was decomposed with ice and dilute sulphuric acid. The decomposition product was subjected to steam distillation, to free it from chloriodo-benzene. The residue was taken up in ether, dried over calcium chloride, filtered and the ether evaporated off. To free the carbinol, which weighed about 25 grams, from any di-brom-benzophenone, it was dissolved in about 30 cc. of benzol, to this a solution of 10 cc. concentrated sulphuric acid in 60 cc. of freshly distilled methyl sulphate was added and the polysulphate[3] left to crystallize.

The crystals were washed with methyl sulphate and benzol, the polysulphate was hydrolyzed, the carbinol taken up in benzol, dried, and crystallized from petroleum ether. The pure carbinol thus obtained weighed 17 grams and melted at 114–5° C.

Analysis:

0.1616 gram of carbinol by ignition with sodium carbonate gave 0.1881 gram AgCl + AgBr; this, on fusing in a current of chlorine lost 0.0323 gram.

	Cl. Per Cent.	Br. Per cent.
Found	7.93	35.91
Calculated for $C_{19}H_{13}OBr_2Cl$	7.83	35.34

[1] Ber., **17**, 1633, 2650 (1884).

[2] Meyer u. Jacobson, Lehrbuch, **2**, 209.

[3] Ber., **40**, 1854 (1907).

Di-p-brom-p-chlor-triphenyl Carbinol Chloride.

Ten grams of the pure carbinol were dissolved in benzol, to which some fused calcium chloride was added, and the solution saturated with gaseous hydrochloric acid. The solution was filtered, and the solvent evaporated off completely *in vacuo*. The carbinol chloride as crystallized from petroleum ether, weighed 10 grams, and melted at 133.5–134.5° C., Gomberg[1] gives the m. p. as 135° C.

Di-p-brom-p-chlor-triphenylanilido Methane.

One gram (2.5 mols.) of freshly distilled aniline were added to a benzol solution of 2 grams of the carbinol chloride. After a day's standing, the solution was filtered from the precipitated aniline hydrochloride. The latter was extracted with hot benzol for part of the anilidomethane, the combined solutions were concentrated *in vacuo*, and the product crystallized from petroleum ether, m. p. 182–183° C. The substance is readily soluble in acetone, ether and chloroform. The acetic acid solution of it turns red.

Analysis:

0.4724 gram substance gave 10.50 cc. nitrogen at 25.5° C. and 733 mm. over 50 per cent. KOH.

	Per cent. N.
Found	2.40
Calculated for $C_{25}H_{18}NBr_2Cl$	2.66

Di-p-brom-p-chlor-triphenylethoxy Methane.

Five-tenths gram of sodium were dissolved in absolute alcohol, this treated with a solution of 2 grams of carbinol chloride, in absolute ether, and boiled with reflux condenser for an hour. Water was then added, the carbinol ether freed from alcohol and sodium chloride by filtration, washed, and dried on a porous plate. The product was dissolved in the least amount of benzene, and crystallized after adding hot petroleum ether. The compound weighed 2 grams, and melted at 195.5–196.5° C.

[1] Ber., **42**, 416 (1909).

The Peroxide.

This was prepared by the method of Gomberg.[1] A benzol solution of 2 grams of the carbinol chloride was treated with about 3 grams of molecular silver, (5–6 times the theoretical amount). Dry air was sucked through the solution until the latter was no more colored on stopping the bubbling of the air. The product was filtered from the silver, the latter washed several times with *warm* benzol, the filtrate concentrated *in vacuo*, and the peroxide crystallized by adding ether to the concentrated benzol solution. The product weighed about 2 grams, and melted at 193–194° C. The substance is insoluble in petroleum ether, and alcohol; slightly soluble in boiling ether. Heating the benzol solution to the boiling point of the solvent gradually decomposes the peroxide.

For comparison, the same compound was prepared from sodium peroxide.[2] Two grams of the carbinol chloride were dissolved in 20 cc. warm benzol, to this was added a 5 per cent. solution of 0.5 gram of sodium peroxide, and the mixture shaken for about 30 minutes. The benzol layer was dried, the solvent evaporated off, and the carbinol peroxide crystallized as already described. The yield being very small, no attempt was made to recrystallize the substance. The crystals melted at 188–189° C.

Unsymmetrical Di-p-brom-p-chlor-tetraphenyl Ethane.

This compound was synthesized by the method of Gomberg and Cone.[3] An ethereal solution of three times the theoretical amount of benzyl-magnesium chloride was treated with a 2 gram benzol solution of the carbinol chloride. After a short warming, the mixture was decomposed with ice and dilute sulphuric acid. The product was subjected to steam distillation to free it from any benzyl chloride. The residue was then taken up in ether, dried, and crystallized from petroleum ether. The yield was quantitative. The crys-

[1] Ber., **37,** 1629 (1904).
[2] *Ibid.*, **37,** 1630 (1904).
[3] *Ibid.*, **39,** 1461 (1906).

tals melted at 188° C. The substance is readily soluble in benzol, acetone; slightly in alcohol.

Analysis:

0.2523 gram of the substance on ignition with sodium carbonate gave 0.2491 gram AgBr + AgCl; this on fusing in a current of chlorine, lost 0.0434 gram.

	Cl. Per cent.	Br. Per cent.
Calculated $C_{26}H_{19}Br_2Cl$	6.73	30.38
Found	6.46	30.90

Di-p-brom-p-chlor-triphenyl Brom Methane.

To a solution of 2 grams of carbinol in the least amount of warm benzol excess of acetyl bromide was added, and then petroleum ether. The carbinol bromide was washed with low boiling petroleum ether, and recrytallized from the same solvent. M. p. 171–172° C.; Gomberg[1] gives it as 174° C.

Analysis of labile bromine:

0.3342 gram of substance gave 0.1206 gram AgBr.

	Br. Per cent.
Found	15.36
Calculated $C_{19}H_{12}Br_3Cl$	15.50

Di-p-chlor-p-brom-triphenyl Carbinol.

This was prepared in the same way as the di-*p*-brom-*p*-chlor derivative. For the Grignard reaction, 2.4 grams of magnesium ribbon were dissolved in an ethereal solution of 30 grams of *p*-chlor-iodo-benzene. The solution was cooled, and then a benzol solution of 11 grams of the methyl ester of *p*-brom-benzoic acid added. After boiling for several hours, the mixture was decomposed as usual, steamed, and the carbinol purified by changing it into the polysulphate, hydrolyzing the latter, and crystallizing the carbinol thus obtained. The carbinol weighed 14 grams and melted at 104° C. Van Slyke[2] gives it as 106° C.

Eleven grams of this carbinol were changed into the chloride, which melted at 122° C.

[1] Ber., **42**, 413 (1909).

[2] Thesis (1907).

The Peroxide.

Two grams of the carbinol chloride were dissolved in benzol, to this, about 3 grams of molecular silver were added, and dry air sucked through the solution, until the latter was no more colored on stopping the bubbling of the air. The warm solution of the peroxide was filtered from the silver, concentrated in *vacuo*, and the peroxide obtained in the form of tiny white crystals. The heated substance turned orange and melted at 180° C. into a deep red liquid.

Unsymmetrical Di-p-chlor-p-brom tetraphenyl Ethane.

0.33 Gram of magnesium ribbon was dissolved in an ethereal solution of 1.8 grams of benzyl chloride. After the metal was completely dissolved, the solution was cooled and treated with a benzol solution of 2 grams of the carbinol chloride. The reaction mixture was decomposed, steamed, and crystallized from petroleum ether. The product weighed two grams, and melted at 180–181° C.

Analysis:

0.2351 gram substance on ignition with sodium carbonate gave 0.2307 gram AgCl + AgBr; this lost 0.0211 gram in a current of chlorine.

	Br. Per cent	Cl. Per cent.
Found	16.12	14.89
Calculated for $C_{26}H_{19}Cl_2Br$	16.59	14.71

Di-p-chlor-p-brom-triphenyl Carbinol Bromide.

Two grams of the carbinol were dissolved in the least amount of benzol, the solution treated with excess of acetyl bromide, and then petroleum ether added. The carbinol bromide was crystallized from the latter solvent. M. p. 160–161° C.

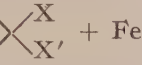
Analysis:

0.2186 gram substance gave 0.0863 gram AgBr.

	Labile Br. Per cent.
Found	16.80
Calculated for $C_{19}H_{12}Cl_2Br_2$	16.97

III. THE DOUBLE SALTS. (INTRODUCTORY).

It has been mentioned in the introduction that the double salts were discovered by Norris and Sanders, and that Gomberg, and Kehrmann and Wentzel, described a variety of these colored compounds. The fact that all these were colored, led Kehrmann to assign to them the quinoid formula

R_2C :  + $FeCl_3$, ($SnCl_4$).

Baeyer, and Gomberg ascribed the color to halochromy, the latter ascribing it, in the case of the carbinol halides to the complex positive triphenylmethyl ion. The success of Gomberg, however, in displacing a nucleus halogen by means of silver sulphate, and in substituting chlorine for bromine in the brominated derivatives of triphenylcarbinol chloride in sulphur dioxide solution, led him to the defense of the quinoid theory.

Baeyer, and Tschitschibabin contended that the quinoid structure of the double salts could not be experimentally defended. They assumed that the quinoid end of the tri-*p*-brom-carbinol chloride and tri-*p*-chlor-carbinol bromide in the ferric chloride double salts being the same, hydrolysis ought to effect in each the splitting off of the same amount of halogen. As experiment did not sustain their assumption, they concluded that the double salts did not exist in the quinoid state.

The object of the following experiments was to verify and extend the work of Baeyer as published in *Ber.* **40,** 3083 (1907).

IV. THE STANNIC HALIDE DOUBLE SALTS.

These were prepared by dissolving the components in dry, thiophene-free benzol, and adding, usually, the solution of the carbinol bromide to that of the filtered solution of the inorganic salt. The crystals were washed by decantation, filtered in an atmosphere of dry air, washed with the solvent, and finally with low boiling petroleum ether.

The analyses were carried out as follows: The weighed

sample was dissolved, usually in acetone, sometimes in ether, and treated with water. Zinc dust was then added, and the mixture allowed to stand over night. The solution was filtered, washed with slightly acid (HNO_3) hot water, until no test for chlorine could be obtained. (In cases where ether had been used to dissolve the carbinol, it was evaporated off before filtering from the zinc dust, care being taken to have the solution alkaline, then acidifying with HNO_3 and filtering.) To the acid filtrate, excess of silver nitrate was added, and the halogens determined in the usual way. Before drying, the silver halide was washed with alcohol, and several times with ether, to make sure of the removal of all traces of organic matter. For trial, the double salt of $(C_6H_5)_3C.Cl$ and $SnCl_4$ was prepared in presence of three times the theoretical amount of stannic chloride.

Analysis:

0.4492 gram substance gave 0.5947 gram AgCl.

	Cl. Per cent.
Found	32.74
Calculated	32.87

It was found that, when the double salts of the carbinol bromides with stannic chloride were prepared, the amount of bromine found on analysis, varied in the different samples. Excess of stannic chloride in the preparation of double salts diminished the per cent. of bromine, so that, when the proportion of stannic chloride to the carbinol bromide was as 4 : 1, almost no trace of bromine could be detected in the compounds.

Di-p-chlor-p-brom-triphenylcarbinol Bromide + Stannic Chloride.

This double salt was prepared in presence of about four times the theoretical amount of stannic chloride. The crystals were red, melting completely at 196° C., and decomposing.

Analysis:

0.3251 gram substance gave 0.3278 gram AgCl + AgBr; this lost 0.0022 gram in a current of chlorine gas.

	Labile Cl. Per cent.	Labile Br. Per cent.
Found	24.23	1.22
Calculated for $(ClC_6H_4)_2 \diagdown C.Br.SnCl_4$ / $BrC_6H_4 \diagup$	19.37	10.92
Calculated for $(ClC_6H_4)_2 \diagdown C.Cl.SnCl_4$ / $BrC_6H_4 \diagup$	25.79	0

The mother liquor of the above double salt was next analyzed for its bromine content. This gave 2.9753 gram AgCl + AgBr, which lost 0.0487 gram in a current of chlorine gas. This loss is equivalent to 0.0875 gram of bromine. The 0.6 gram of the carbinol bromide used contained approximately 0.10 gram of labile bromine. The bromine as found in the analysis of the sample of the double salt, and of the mother liquor amounts to 0.0915 gram. If to this were added the bromine contained in the double salt not analyzed, all of the labile bromine originally present in the carbinol is accounted for. It is clearly seen from the last example that almost complete substitution of the labile bromine had taken place.

The following table gives the results of the analyses of some double salts.

TABLE I.

Substances used.	Approximate mol. proportions	Labile Bromine found.	Labile Bromine calc.	Labile Cl found.	Labile Cl calc.
$(C_6H_5)_3C.Br,SnCl_4$	1 : 1 +	9.98	13.69	25.23	24.28
$(C_6H_5)_3C.Br, SnCl_4$	1 : 3	0.99	13.69	31.32	24.28
$(C_6H_5)_3C.Cl, SnBr_4$	4 : 1	33.17	44.59	6.59	4.95
		33.21	...	6.53	...

Labile chlorine in $(C_6H_5)_3C.Cl.SnCl_4$ = 32.87 per cent.

It is to be noted that in the last analysis, the conditions of experiment were reversed, and that an excess of carbinol chloride was treated with stannic bromide.

A benzol solution of 3 grams triphenylcarbinol chloride was treated with a 10-gram solution of stannic bromide. The crystals were yellowish red, began to soften at about 130° C. and melted completely at 170° C. with decomposition.

Analysis:

	Br.		Cl.		
	I.	II.	I.	II.	Sn.
Found	45.87	45.97	4.09	3.95	16.43
Calculated	44.59	....	4.94		16.59

Four grams of the above double salt were next shaken with 5 grams $SnBr_4$ (in benzol solution) for four days, and again analyzed.

	Br.		Cl.		
	I.	II.	I.	II.	Sn.
Found	47.64	47.46	2.80	2.90	16.03
Calc. for $(C_6H_5)_3C.Cl.SnBr_4$	44.59		4.94		16.59
Calc. for $(C_6H_5)_3C.Br.SnBr_4$	52.48		0		15.62

V. FERRIC CHLORIDE DOUBLE SALTS.

Baeyer prepared these by dissolving the carbinol chloride, or bromide, in a little chloroform by warming, and then treating it with a hot concentrated solution of the *calculated* amount of ferric chloride in acetic acid. This method would not work in the preparation of the double salt of the *simple* triphenylbrommethane.

The method used in these experiments, was to dissolve the components in absolute ether and add, usually, the solution of the carbinol bromide to that of the filtered iron salt solution. The crystals were either washed by decantation or filtered in dry air and dried *in vacuo*. The analyses show that the per cent. of iron was in every case about a per cent. too high. This might be explained on the assumption that more or less of the iron salt was occluded in the double salt which separates out immediately. The ferric chloride used was Kahlbaum.

The method of analysis was the following: The sample was either dissolved in acetone (Baeyer), and treated with water which contained a few drops of nitric acid, or hydrolyzed directly with water alone which also contained a few drops of nitric acid. The solution was filtered from the carbinol, the iron precipitated in the filtrate by ammonia and the halogens estimated in the last filtrate.

The double salt, prepared by using approximately equimolecular quantities of the components, triphenylcarbinol

bromide and ferric chloride, separated out in brick-red crystals, which began to soften at 145° C. and melted completely at 155° C.

I. 0.5145 gram substance gave 0.0922 gram Fe_2O_3. II. 0.5460 gram substance gave 0.0980 gram Fe_2O_3; 0.6951 gram AgCl + AgBr; this lost 0.0450 gram in a current of chlorine gas.

	Labile Cl.	Labile Br.	Fe	
	Per cent.	Per cent.	Per cent.	Per cent.
Found	22.88	14.80	12.52	12.55
Calculated for $C_{19}H_{15}Br.FeCl_3$	21.93	16.46	11.51	

The following table gives the results of analyses carried out on double salts of triphenyl carbinol bromide and ferric chloride.

TABLE II.

	Labile Br		Labile Cl		Iron.	
Approx. mol prop.	Found.	Calc.	Found.	Calc.	Found.	Calc.
1. $(C_6H_5)_3C.Br : FeCl_3$ :: 1 : 2	11.91	16.46	24.24	21.93	12.70	11.51
	11.81	. .	25.10	. . .	12.57	. . .
2. $(C_6H_5)_3C.Br : FeCl_3$ :: 1 : 4	5.76	16.46	28.77	21.93	13.29	11.51
	5.80		28.70		13.27	
3. $(C_6H_5)_3C.Br : FeCl_3$ :: 1 : 4	10.50	16.46	25.64	21.93	12.87	11.51
	10.51		25.74		12.88	

The marked difference in the percentage of bromine and chlorine in the last two analyses is due to the fact that in the first, the solution of ferric chloride was added to that of the carbinol bromide, while in the last, the carbinol bromide was added to the excess of ferric chloride.

The following two analyses were made on the double salts of tri-*p*-chlor-triphenyl carbinol bromide with ferric chloride. In the first, the molecular proportions were approximately 1 : 1; in the second as 1 : 3, 5. The double salts were prepared according to the method of Baeyer, by adding the warm concentrated chloroform solution of the carbinol bromide to the hot acetic acid solution of ferric chloride.

TABLE III.

	Bromine.		Chlorine.		Iron.	
	Calc.	Found.	Calc.	Found.	Calc	Found.
1.....	13.58	12.34	18.08	18.89	9.49	10.24
		12.58		18.73		10.26
2.....	13.58	5.06	18.08	23.48	9.49	10.18
		5.35		23.45		...

The double salts in *ether* soon decomposed into a black, non-crystalline product. On account of this, the double salts were never allowed to stand in contact with the solvent more than ten minutes.

VI. STABILITY OF PARA BROMINE.

The above observed tendency of the inorganic chloride to take up the bromine from the carbinol, was next put to test in another direction. It was thought that, by properly controlling the experimental conditions, it might be possible to replace the bromine atom already in the nucleus by chlorine, as has already been observed in the case of the carbinol-bromine. This assumption was based on the possibility of ferric chloride acting in the same sense as silver chloride did in the experiments of Gomberg with the carbinol halides in sulphur dioxide.

Accordingly, the double salt of tri-*p*-bromtriphenyl-carbinol chloride-ferric chloride was prepared in presence of three times the required quantity of ferric chloride in chloroform and acetic acid. The crystals were red, melting completely at 233° C.; Baeyer gives it as 237° C. No bromine was found in the double salt. 1.6 Grams of the same compound were shaken for six days with a solution of 3 grams ferric chloride in acetic acid. The crystals of the dried double salt melted completely at 228° C. Analysis in this case, too, did not show any trace of bromine.

To be absolutely sure that no nucleus bromine was substituted by chlorine, the carbinol obtained from the last analysis, was analyzed for its halogen content. This did not give any better results.

The conditions of the experiment were again modified. This time the double salt, tri-*p*-chlor-triphenylcarbinol

bromide-zinc bromide in acetic ester, was prepared. Zinc bromide was the component used in excess. The crystals were brick-red, began to soften at 215° and melted completely at 230° C.

Analysis:

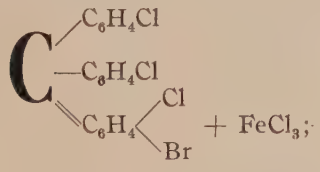
I. 0.4824 gram substance gave 0.4153 gram silver halide, this lost 0.0971 gram. II. 0.4627 gram substance gave 0.0610 gram ZnO.

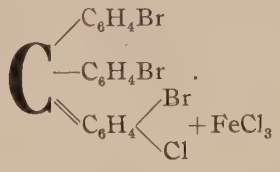
	Cl.	Br.	Zn.
Found	0.84	36.16	10.58
Calculated	0.0	36.80	10.03

A portion of the same double salt in acetic ester was then shaken for six days with excess of zinc bromide. The crystals melted from 215–229° C. The salt was hydrolyzed and the carbinol analyzed for its halogen content. No bromine could be detected.

VII. CONCLUSION.

The results, obtained in the analyses of the double salts, confirm the contention of Baeyer that no nucleus halogen can be broken off by hydrolyzing these compounds. Baeyer, however, premised that the double salts of a carbinol bromide and a carbinol chloride with $FeCl_3$ would have the same quinoid end, and expected that on hydrolysis they ought to behave alike. He assumed the correctness of the following two formulae:

(1) 

(2) 

Experiment has shown that formula (1) is not correct, because the double salt corresponding to it contains less bromine than the theoretical.

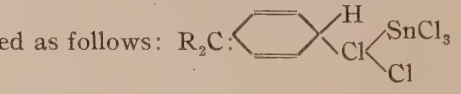
To be sure, Aickelin obtained theoretical results, but these were due to the fact that he used equimolecular quantities of the compounds. Experiment does not tell in what form these double salts exist.

A double salt of $(C_6H_5)_3C.Br$ and $SnCl_4$ was prepared, which, on analysis, gave 9.84 per cent. bromine. When a portion of the same double salt was shaken for three weeks with an excess of $SnCl_4$, no trace of bromine could be detected.

In the case of the experiment with four times the molecular quantity of the $(C_6H_5)_3C.Cl$, and $SnBr_4$, again too low results for bromine were obtained. While, when the $SnBr_4$ was used in excess, the per cent. of *chlorine* was too low.

Discarding, for the present, the quinoid structure, it might be supposed that the equilibrium exists between the carbinol halogen and the inorganic component. In that case, we would have the mixed salts of the types: $(C_6H_5)_3C.Cl.SnCl_4$ and $(C_6H_5)_3C.Br.SnCl_4$, etc. Excess of $SnCl_4$, taking the last example, would disturb the equilibrium in the sense that finally the homogeneous compound $(C_6H_5)_3C.Cl.SnCl_4$ would be left—provided this is less soluble than $(C_6H_5)_3C.Cl.SnBr_4$.

But then the question could be asked: why is it that in the case of tri-*p*-brom-tri-phenylcarbinol chloride-ferric chloride, where by quinoidation one of the *p*-bromine atoms becomes labile, no such bromine can be replaced by chlorine? The answer is again in terms of negatives.

Comparing the reactivity of a carbinol halogen with that of one in the quinoid nucleus, it is found that the carbinol halogen is by far the more reactive. Whereas, silver in silver sulphate will immediately take up the carbinol halogen in any solvent, the double transposition, as found by Gomberg in the case of a *p*-halogen atom after quinoidation, takes a good many days. If then the double transposition in the double salt takes place before quinoidation, *a priori* there is no reason to suppose that the *p*-bromine atom should also be replaced by chlorine under the influence of ferric chloride, or stannic chloride. Again, according to Stieglitz, the constitution of the double salt of triphenyl carbinol chloride is to be expressed as follows: 

with the "wandering" chlorine atom as trivalent. *As bromine has a greater tendency to assume the bromonium form than chlorine the chloronium, it is possible that in the brominated derivatives the stannic chloride wander from the chlorine to the bromine atom after quinoidation, and then this atom assuming the trivalent state would not be replaceable by chlorine, no matter how much of the inorganic salt is present.*

It was in this way that D. Van Slyke[1] explained the inhibitive effect of sulphuric acid on the removal of the *p*-halogen atoms in the quinoid nucleus by silver sulphate.

As for the objection that the assumption of a trivalent halogen atom, would lead to the assumption of a trivalent hydrogen atom, it can be said that there is no such necessity as after quinoidation, the inorganic salt would attach itself to the halogen. If it were possible to prepare a double salt of the simple hydrocarbon triphenylmethane, then would the objection be valid.

VIII. ANISYL DERIVATIVES OF TRIPHENYLCARBINOL.

Baeyer and Villiger,[2] while studying the basic properties of oxygen, have also investigated the oxygen derivatives of triphenylmethane. Having observed that the "oxonium salts" of dibenzalacetone were intensely colored, they investigated the relation of color and chemical constitution from this point also.

Because they had observed[3] that tertiary alcohols possess strong basic properties, they expressed the opinion that the colored solution of a carbinol in a mixture of acetic and sulphuric acids might contain the oxonium salt of the carbinol.

Baeyer and Villiger then introduced anisyl groups into the benzene nuclei, and observed that trianisyl carbinol forms crystalline salts. They then concluded that trianisyl carbinol is a halochromic substance, whose deep color in combination with acids was not due to a chromophore group but to the properties of the complex body taken as a whole.

By introducing the methoxyl groups in different positions

[1] Thesis (1907).

[2] Ber., **35**, 1189.

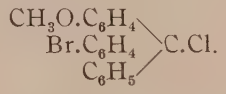
[3] *Ibid.*, **34**, 2679.

in the benzene nucleus, the same observers found[1] that the influence of the anisyl groups was greatest in the para position.

We have prepared a few of the anisyl derivatives of triphenyl carbinol with the object of studying the effect of the oxygen on the course of quinoidation.

IX. SYNTHESIS OF OXYGEN DERIVATIVES OF TRIPHENYL CARBINOL.

P-methoxy-p-brom-triphenyl Carbinol Chloride,



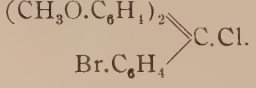
—This product was synthesized by means of Grignard's reaction. 1.45 Grams magnesium were dissolved in an ethereal solution of 15 grams *p*-anisyl-iodide. The solution was cooled, treated with an ethereal solution of 15 grams *p*-brom-benzophenone, and boiled for several hours. The reaction mixture was decomposed as usual, steamed, the carbinol taken up in ether, washed with dilute sulphuric acid, then potassium hydroxide, and dried. The carbinol could not be crystallized. Accordingly, it was taken up in benzol, and the solution over calcium chloride saturated with hydrochloric acid gas. The carbinol chloride was crystallized from petroleum ether. The crystals were slightly pink in color. M. p. 97° C. The yield was 12 grams.

Analysis:

I. 0.2855 gram substance required 7.24 cc. $N/10$ $AgNO_3$.
II. 0.3274 gram substance required 8.22 cc. $N/10$ $AgNO_3$.

	Chlorine.	
	I.	II.
Found	8.99	8.90
Calculated	9.15	

Di-p-anisyl-p-brom-triphenyl Carbinol Chloride,



[1] Ber., **35**, 3013.

—Three grams magnesium were dissolved in the course of a day in an ethereal solution of 30 grams *p*-anisyl-iodide. The solution was cooled and treated gradually with an ethereal solution of *p*-brom-benzoate, and boiled for several hours. The reaction mixture was treated in the same way as the monoanisyl derivative.

The oily carbinol was dissolved in benzol and saturated with hydrochloric acid gas. The first few bubbles of the acid turned the benzol solution deep red. Evidently the dichloride was formed. According to Baeyer,[1] the oxygen of the methoxyl group in the trianisyl unites with one molecule of the acid to give the *colored* oxonium hydrochloride. The dichloride separated out as an insoluble oil. This was warmed and dry air was passed through the benzol solution until all the oil went into solution. The solvent was evaporated off, and the carbinol chloride crystallized from petroleum ether, to which a few cc. of acetyl chloride were added.

The recrystallized carbinol chloride melted at 122–122.5° and was slightly pink in color. The purified product weighed 14 grams.

Analysis:

I. 0.3429 gram substance required 7.95 cc. $N/10$ $AgNO_3$.
II. 0.4030 gram substance required 9.34 cc. $N/10$ $AgNO_3$.

	Chlorine.	
	I. Per cent.	II. Per cent.
Found	8.21	8.22
Calculated	8.49	

It was found by Van Slyke[2] that in the case of the sulphates para-bromine directs the quinoidation to the nucleus in which it is situated and that even when there are "two para-chlorine atoms to one of bromine, the quinoidation takes place almost entirely in the brominated nucleus." He also showed that orthobromine "loses its influence to direct the quinoidation toward its own nucleus."

Gomberg found that a chlorine atom in the nucleus of

[1] Ber., **35**, 1189 (1902).
[2] Thesis.

the phenylated Xanthone derivative, which nucleus was not linked to the xanthone oxygen, could not be replaced by the fluorine of silver fluoride in sulphur dioxide. Evidently, the chlorinated nucleus was not changed into the desmotropic quinoid modification.

X. TAUTOMERIZATION OF THE ANISYL CHLORIDES.

The benzol solutions of the carbinol chlorides, when shaken with silver chloride, did not show any substitution of chlorine by bromine. When, however, the same carbinol chlorides were dissolved in sulphur dioxide, the solutions were colored cherry-red in the case of the mono-anisyl, and dark red in that of the dianisyl derivative. Here, as in the case of the simple halogenated derivatives of the carbinol chlorides, tautomerization did take place.

The method of experimentation was that of Gomberg.[1] A weighed amount of the carbinol chloride was introduced in a hard glass tube, about 0.5 gram of AgCl was added, and then dry SO_2 was condensed in the tube. The latter was then sealed and shaken on the machine. For the analysis, the tube was opened, after it stood in the freezing mixture for some time, the sulphur dioxide allowed to evaporate and the remnants were washed with hot benzol and ether. The residue was taken up in cold concentrated ammonia, filtered, boiled to drive away most of the ammonia, acidified with nitric acid and the halogen content determined as usual.

Mono-*p*-anisyl-mono-*p*-brom-triphenyl carbinol chloride was shaken with AgCl for three months.

Analysis:

I. 0.3980 gram substance; 0.5410 gram AgCl + AgBr, this lost 0.0388 gram in a current of chlorine gas. II. 0.2948 gram substance; the silver halide lost 0.0284 gram in Cl_2 current.

	Br.	
	I.	II.
Found	17.51	17.31
Calculated for $C_{20}H_{16}OBrCl$	20.63	

[1] Ber., **40**, 1859 (1907).

Di-*p*-anisyl-*p*-brom-triphenylcarbinol chloride was shaken with AgCl for 100 days.

Analysis:

I. 0.3024 gram substance; the silver halide lost 0.0091 gram in Cl_2 current. II. 0.3263 gram substance; the silver halide lost 0.0109 gram in Cl_2 current.

	Br.	
	I.	II.
Found	5.41	6.00
Calculated for $C_{21}H_{18}O_2BrCl$	19.14	

The monoanisyl carbinol chloride was next dissolved in benzol and shaken with about 3 grams of molecular silver.

The experiments were done according to the directions given by Gomberg.[1]

Mono-p-anisyl-mono-p-brom-triphenylcarbinol Chloride.

Analysis:

I. 0.3056 gram substance; 0.1455 gram AgCl + AgBr; this lost 0.0079 gram in Cl_2 current. This sample was shaken for three weeks. II. 0.3928 gram substance; 0.1723 gram AgCl + AgBr; this lost 0.0066 gram in Cl_2 current. This sample was shaken for ten days.

	Br.		Cl.	
	I.	II.	I.	II.
Found	4.64	3.02	9.07	9.08
Calculated for $C_{20}H_{16}OBrCl$	20.63		9.15	

Gomberg[2] found that, after a week's shaking of the sulphur dioxide solution of mono-*p*-bromtriphenylcarbinol chloride with silver chloride, nearly a whole molecule of bromine had been substituted by chlorine.

In our case, the para-bromine is found not to be so easily substituted by chlorine. Especially is this evident in the case of the dianisyl derivative.

Also, Gomberg[3] found that molecular silver will abstract from the simple mono-*p*-brom-carbinol chloride (in benzol solution), nearly 1/5 of one molecule of bromine in one day, and 1/2 a molecule in 79 days.

[1] Ber., **39**, 3293 (1906).

[2] *Ibid.*, **40**, 1862 (1907).

[3] *Ibid.*, **39**, 3294 (1906).

In the case of the *p*-brom-mono-*p*-anisyl carbinol chloride, three weeks' shaking showed an abstraction of 22 per cent. of one molecule of bromine.

The conclusion is that the methoxyl groups tend to direct the quinoidation to the para-anisylated nuclei.

XI. SUMMARY.

1. A number of new derivatives of para halogenated triphenyl carbinol have been synthesized.

2. A number of new double salts of the para-halogenated carbinol halides have been prepared.

3. It was found that the double salts of the *carbinol bromides* with ferric chloride (or stannic chloride) behaved abnormally. The carbinol bromine content of these varied with the concentration of the metallic chloride. It was therefore, possible by using enough of the inorganic component to obtain the homogeneous carbinol chloride + inorganic chloride double salt.

4. An explanation was thus given of the negative results of Baeyer by pointing out that the salts formed, by treating a carbinol bromide and a carbinol chloride with the same inorganic component, did not contain the same quinoid end of the molecule, and hence could not be expected to behave alike.

5. It was found that excess of the metallic chloride did not substitute a para-bromine atom for chlorine. The attempt was made to assign this to the difference in the reactivity of the carbinol and a para halogen in the quinoid nucleus—the latter, according to Gomberg, being far less reactive than the carbinol halogen.

6. According to Stieglitz, the halogen atom, which links the inorganic component to the organic radical, becomes trivalent, consequently such a halogen atom ought to behave differently from monovalent bromine, as chlorine in sodium chloride does from that in the chlorates, where it is not readily precipitated in the presence of silver nitrate, etc. An explanation was then given for the stability of the para-bromine atom in the double salt on the basis that bromine had a

greater tendency than chlorine to assume the trivalent state, and that in the process of quinoidation the *bromine atom* became the linking medium between the two components, and was thus protected from the action of $FeCl_3$ ($SnCl_4$, etc.).

7. According to Baeyer, the assumption of a trivalent halogen atom would necessitate the assumption of a trivalent hydrogen atom. It was shown that no such necessity existed.

8. Two new *p*-anisyl-*p*-brominated triphenyl carbinol chlorides have been synthesized.

9. It was found that the anisyl groups directed the quinoidation to the nuclei in which they themselves were situated.